in either one or both of these reactions. The position of equilibrium is well-known to favor the *trans*-isomer. This fact, and the comparatively slow rate of conversion of *trans* acids to *cis* acids may reflect, at least in part, the slower rate of oxygen attack upon the *trans* configuration.

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Search for New Industrial Oils. IX.
Cuphea, a Versatile Source of Fatty Acids

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Abstract

Seed oils from five species of *Cuphea* show three distinct patterns of fatty acid composition. *C. hookeriana* and *C. painteri* oils contain ca. 70% caprylic acid, *C. ignea* and *C. llavea* oils have over 80% capric acid, and *C. carthagenensis* oil contains 57% lauric and 18% capric acids.

Introduction

THE FIRST REPORT of a high concentration of capric acid in seed oil of herbaceous plants was based on the discovery early in this survey that oil from seed of *Cuphea llavea* var. *miniata* contained over 80% (2) of this fatty acid component. Earlier known sources of capric acid containing comparable concentrations were oils from *Ulmus americana* (4), *Zelkova serrata* (5), and more recently other species of *Ulmus* (10) and *Sassafras albidum* (2).

The present commercial source of capric, caprylic, and lauric acids is coconut oil imported from the tropics (6). These acids of intermediate chain length are highly important to the chemical industry as raw material for the production of surface-active agents, plasticizers, physiologically active compounds, perfumes, and flavors. In 1962 the United States imported 807 million lb of lauric acid oils, ca. 90% of which came from coconuts (12). A domestic source of capric and lauric acids could be of great strategic importance and, if sufficiently economical, could prove of value to the chemical industry in normal times. Accordingly, special attention was given to the recollection of *C. llavea* and to collection of other species of the genus.

Cuphea of the family Lythraceae is a large genus of over 200 species of herbs and shrubs in the tropics and subtropics of the Americas. Varieties of *C. ignea,* cigar flower, and *C. llavea,* cinnabar cuphea, are popular ornamentals in warmer sections of the United States.

Materials and Methods

Samples were prepared and analyzed as described previously (3). Methyl esters were derived from the oils by methanolysis catalyzed by HCl. Analysis by gas chromatography (GLC) followed previously reported procedures (8).

Evaporation of solvents under a stream of nitrogen on a steam bath gave low yields of recovered ester, and GLC analyses of methyl esters gave low values for acids having less than 10 carbon atoms in chain.

To avoid losses of lower mol wt methyl esters from *C. hookeriana* and *C. painteri,* the following modification of the usual procedure was used. Ethyl ether was used in place of benzene to increase the solubility of oil in the methanol-HCl reagent. After methanolysis, solvent removal was accomplished by fractional distillation through a column packed with glass helices. Removal of the ether was essentially complete with no detectable loss of fatty acids as determined by weighing the esters and examining the GLC curve for evidences of residual solvent. Other means of avoiding such losses have been reported recently (1,7,11).

Results and Discussion

All five species of *Cuphea* analyzed produce seed oils rich in intermediate chain-length acids, but three distinct patterns of composition are noted (Table I). Three accessions of *C. llavea,* including the previously reported sample (2) and one of *C. ignea,* produce oil with more than 80% capric acid. Oils from seeds of *C. hookeriana* and *C. painteri* contain ca. 70%

TABLE I

Analytical Data on *Cuphea* Seeds and Derived Oils

	C. carthagenensis	*C. hookeriana*	*C. painteri*	*C. ignea*	*C. llavea*[a]
Seed analysis					
Weight/1,000, g	0.7	0.3	0.5	1.0	1.0; 3.3; 0.9
Protein (N × 6.25), % DB	16	19	23	18	17; 21; 15
Oil, % DB	33	16	36	34	21; 30; 17
Oil analysis					
Iodine value[b]	18	18	12	10	18; 12; –
Percent methyl ester in mixed methyl esters (by area on GLC curve)					
6:0	....	0.1	0.2	....	....
8:0	3	65	73	3	0.8; 0.6; 1
10:0	18	24	20	87	83; 85; 86
12:0	57	0.1	0.2	0.8	1; 3; 1
14:0	8	0.2	0.3	0.2	0.8; 1; 0.6
16:0	3	2	2	2	3; 2; 2
18:0	0.6	0.5	0.4	....	0.5; 0.3; 0.5
18:1	5	2	2	2	5; 4; 2
18:2	5	6	2	4	6; 4; 4
18:3	....	0.4	....	....	tr; –; –

[a] One of these samples is the one previously reported (2).
[b] Approximately 0.2 g samples used.

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[2] ARS, USDA.

caprylic acid. *C. carthagenensis* provides an oil richer in both lauric and capric acids than coconut oil. Only from the original sample of *C. llavea* has the major component been isolated and rigorously characterized by derivative formation (13). However, the GLC data indicating the presence of these saturated acids in the closely related species leave little doubt as to their identity.

Any of the oilseeds from the five species reported here should be amenable to present processing methods of oil recovery and preparation of intermediate chain-length acids from the glycerides. A recent patent demonstrates one procedure for preparing decanoic acid from *C. llavea* oil (9). These oils should find ready acceptance by industry if suitable strains of *Cuphea* can be found or agronomically developed to permit production of the seed economically enough to make the oil available at a competitive price.

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Recent Research on Sesamin, Sesamolin, and Related Compounds[1]

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Abstract

This review covers the literature on sesamin, sesamolin and related compounds published since 1951. The topics reviewed include structural considerations, natural occurrence, influence of oil processing, analytical methods, isolation procedures and commercial preparations, various biological effects and stability questions.

Recent developments in pyrethrum synergists are discussed at length, since they owe so much to the discovery of the synergistic activities of sesamin and sesamolin.

Introduction

THE SEED OIL OF *Sesamum indicum*, commonly known as sesame oil, contains two minor constituents, sesamin and sesamolin, which are responsible for its characteristic color reactions, its insecticidal synergism and some other specific properties. Sesamol, a phenolic antioxidant, usually present in traces, is formed from sesamolin under certain processing conditions.

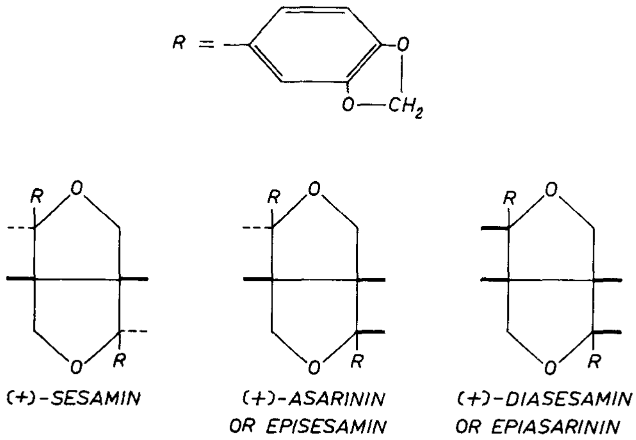
A critical survey of the literature on sesamin, sesamolin and sesamol was included in a 1951 review on sesame oil (1). The purpose of the present paper is to review work carried out since then on these and related compounds.

Structural Considerations

Sesamin is 2,6-(3,4-methylenedioxyphenyl)-*cis*-2,7-dioxabicyclo-[3.3.0]octane. Its synthesis has been reported from three laboratories (2–4). According to its formula, three stereoisomers are theoretically possible, each existing in two enantiomorphic forms. Sesamin and asarinin constitute two members of this series. The third member was discovered recently by Beroza (5) and termed epiasarinin by him. The structures of these compounds have been elucidated (5–8) and absolute configurations assigned to them as shown in Figure 1.

Recent nuclear magnetic resonance measurements on sesamin and asarinin led Govil, Kanekar, and Khetrapal (9) to suggest that the structures assigned to sesamin and epiasarinin should be interchanged. In the course of a study of the stereochemistry of some new lignanes carried out about the same time, Weinges (10) also measured the NMR spectra of sesamin and asarinin. His results confirmed the previously established configurations. Becker and Beroza (11) used the same technique not only on sesamin and asarinin, but also on epiasarinin, and similarly found no reason to alter the conclusions assigning to these three stereoisomers the structures shown in Figure 1.

The structure of sesamolin has been established as that of 2-(3,4-methylenedioxyphenoxy)-6-(3,4-methylenedioxyphenyl)-*cis*-3,7-dioxabicyclo [3.3.0] octane (Fig. 2a), with the same tetrahydrofurfurofuran nucleus as in sesamin (8,12,13). Sesamolin differs from sesamin by the presence of a connecting oxygen atom between the tetrahydrofurfurofuran nucleus and one of the methylenedioxyphenyl groups. This makes sesamolin an acetal-type derivative of sesamol (Fig. 2b), as suggested earlier by Boeseken, Cohen and Kip



(+)-SESAMIN (+)-ASARININ OR EPISESAMIN (+)-DIASESAMIN OR EPIASARININ

FIG. 1. Absolute configuration of the dextrorotatory stereoisomers of the sesamin series (6).

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